

## SPOTLIGHTING MOLECULES ON SURFACES

### LOOKING AT CHEMICAL BONDING ATOM BY ATOM

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Chemical reactions at surfaces play central roles in such economically important processes as the catalysis of chemical production, corrosion, the fabrication of computer chips, the behavior of biomaterials, and the fate of contaminants in the environment. Chemical bonding of atoms and molecules to the surface (adsorption)—the first step in many such reactions—occurs when some of the electrons that are less tightly bound to atomic nuclei (valence electrons) rearrange themselves. Because of this loose binding, the valence electrons can be shared by several atoms, forming molecular orbitals. How these orbitals are distributed, on the atoms and along different bond directions, and what energies the electrons in the orbitals can have are some of the details that we would like to know.

#### X-RAY EMISSION SPECTROSCOPY

To observe the orbitals involved in the surface chemical bond is an experimental challenge because of the much larger number of atoms in the solid below the surface (substrate). What we need is a method that allows us not only to separate out the orbitals on the adsorbed entity (adsorbate) but also to spotlight one atom at a time. This tall order can be filled by using x-ray emission spectroscopy (XES), also called x-ray fluorescence spectroscopy, in which the absorption of an x ray is followed by the emission of a fluorescence x ray at a different wavelength.

Though simple sounding, x-ray emission yields the information we seek. The wavelength of the incoming x ray identifies which atom is absorbing, since atoms of different elements (or the same element in distinct chemical-bonding environments) absorb at characteristic wavelengths. Similarly, the wavelength of the fluorescence x ray identifies the

molecular orbital, and the intensity of the fluorescence indicates how much of the orbital is around the absorbing atom. Additional information about the orientation (symmetry) of the orbitals comes from measurements made at various angles relative to the surface of the incoming and fluorescence x rays. Finally, since the fluorescence comes only from the adsorbate, there is no obscuring signal from below the surface.

XES applied to surfaces is extremely demanding owing to the considerable inefficiencies associated with the creation and detection of fluorescence x rays and with the low adsorbate concentration. It is only recently that the field has begun to be exploited, thanks to the appearance of third-generation synchrotron radiation sources, such as the ALS, whose high brightness makes it possible to overcome these limitations.

#### ADSORBATES ON METAL SURFACES

In experiments at Beamline 8.0.1, our group has used XES to examine a sequence of increasingly complex molecules on metal surfaces, beginning with molecular nitrogen ( $N_2$ ) and carbon monoxide (CO) on nickel and copper. We have discovered new details about the bonding between these molecules and the surface, which show that surface bonding involves not only new orbitals derived from both the adsorbate and the substrate, but also rearrangements within the orbital structure of the molecule itself. We are now moving on to large molecules of the type that are common in biological materials and in the environment.

Adsorption of a simple amino acid, such as glycine ( $NH_2CH_2COOH$ ), on copper [specifically, the Cu(110) surface] provides a simple example. The Cu(110) surface has twofold symmetry, in which the surface atoms are lined up in rows and the glycine molecule adsorbs in an orientation perpendicular to these rows with both ends of the molecule bonding

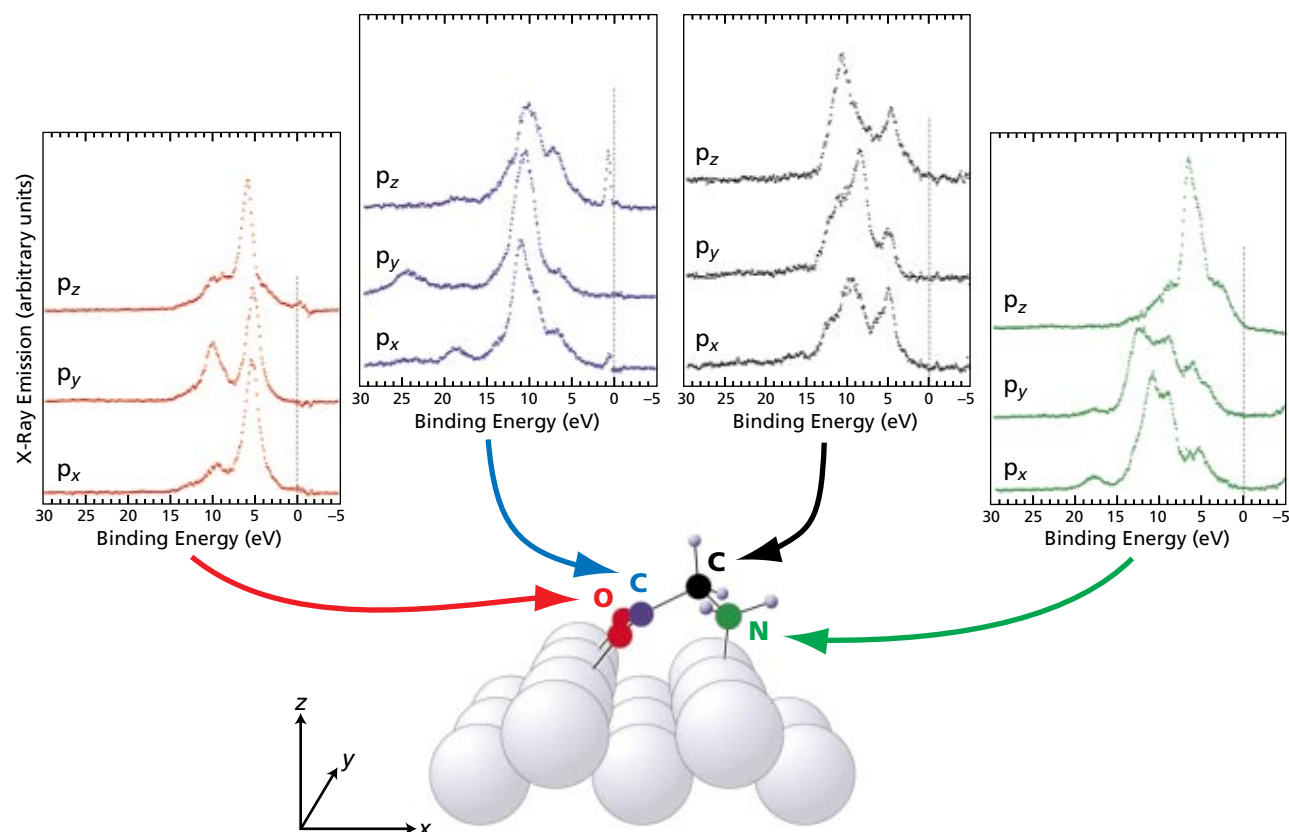
to the surface. Combining experiment with theoretical calculations, we can now study how molecular orbitals of a specific symmetry are distributed over different atomic sites in a complicated molecular adsorption complex.

### LIQUID INTERFACES

With the successful development of XES for surfaces and interfaces, we see a unique opportunity for a new application of these methods to liquid interfaces, since x-ray-in/x-ray-out spectroscopies do not require samples to be in a vacuum. For example, a new interdisciplinary field, referred to as molecular environmental science, has emerged in the last few

years in response to the need for basic research to underpin long-term solutions to environmental problems. It is clear that many of the reactions involving contaminants take place at liquid-solid interfaces, and we expect that XES will make a major contribution to understanding some of these important processes.

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X-ray emission spectra from the amino acid glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) adsorbed on copper [specifically, the Cu(110) surface] were taken at different angles relative to the surface. These spectra were combined to decompose the molecular orbitals associated with the oxygen atoms, each of the two carbon atoms (which have different chemical environments), and the nitrogen atom into the components labeled  $p_x$ ,  $p_y$ , and  $p_z$ , which have different symmetries and energies. For a complete understanding of the molecular orbitals for complicated adsorbates of this type, experimental data must be compared to theoretical calculations.